# HIGH YIELD MAGNETIC NANOPARTICLES FILLED MULTIWALLED CARBON NANOTUBES USING PULSED LASER DEPOSITION.

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## ABSTRACT

We present a high yield filling technique of multi-walled carbon nanotubes (MWCNTs), grown vertically on a $SiO_2$ substrate, with magnetic nanoparticles using pulsed laser deposition (PLD). Magnetization measurements in-plane and out-of-plane with respect to the sample surface indicate reasonable coercivity estimated at 0.4 T. The magnetic anisotropy is however found to be randomly oriented, indicating a polycrystalline structure. The unique difference between the in-plane and out-of-plane magnetizations is the sharing produced by the demagnetizing field in the perpendicular direction.

## 1. INTRODUCTION

Since its discovery in the early 1990s [1] (Iijima, 1991), there has been exponential increase in research on carbon nanotubes (CNTs) due to its potential for applications in a wide range of technologies. CNTs are cylindrical tubes of rolled graphene with diameter ranging from 1 to 2 nm and several μm in length. Based on their chirality CNTs come in three different forms a metal, a semi-metal and a semiconductor as illustrated in Figure 1.

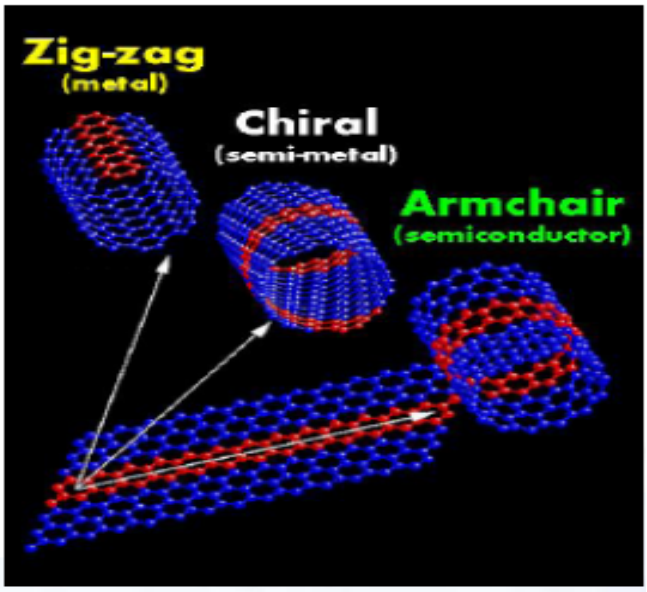


**Fig. 1 The three forms of CNTs based on chirality meta, semi-metal, and semiconductor.**

Of particular interest has been to realize CNTs impregnated with functional materials, such as the magnetic nanoparticles. CNTs filled with functional materials give rise to hybrid materials such as ferromagnetic and semiconductor material which is of interest in new generation electronics and data storage devices. A major difficulty in filling single-walled (SW) CNTs is the low dimensionality of the tube diameter, which is close to 1 nm. Another difficulty is the fact that the driving forces of nanocapillarity are not well understood. The low-dimensionality issue is generally overcome in the case of MWCNTs where the tube diameter could range from 10 to 50 nm inner diameter and 20 to 70 nm outer diameter even though the driving forces of capillary filling are similar to that of SWCNTs. This has led to successful filling of MWCNTs by magnetic materials using various methods. For example, ferrite nanowires were synthesized by vigorous stirring of an aqueous solution, containing cobalt and iron nitrates together with MWCNTs [2] (Keller et al., 2004) and MWCNTs were also filled with nickel and uranium oxides using a chemical method [3] (Tsang et al, 1994). Here, we describe a chemical approach to fill MWCNTs by a magnetic material in order to develop synthesized nanosize magnets. Nanomagnets are important as vital component in nano-electromechanical systems (NEMS) and have potential applications ranging from medicine to defense [4,5]. (Wu et al, 2004; Yoshida et al 2002).

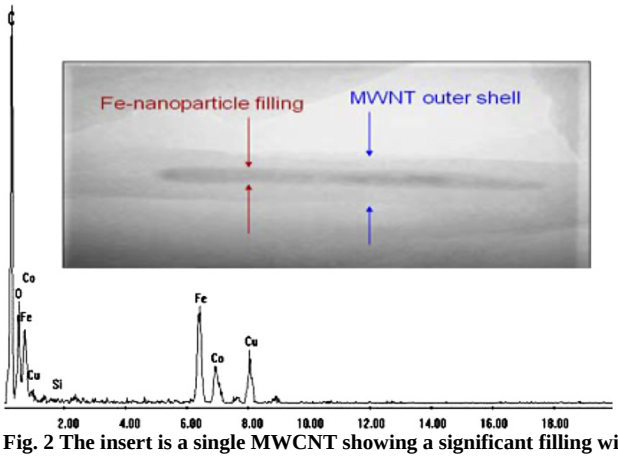


**Fig. 2 The insert is a single MWCNT showing a significant filling with outer diameter _30nm and inner diameter _10nm filled with Fe nanoparticles. Energy-dispersive X-ray graph shows Fe peaks due to the filling material inside the tube shown on the insert as a dark background.**

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In Figure 2 a typical filled MWCNT is shown at $10^6$ magnifications. The length of the filling which shows up as a region of darker contrast in the image is 180 nm with a diameter of 9 nm. Energy-dispersive X-ray of the filled MWCNT shows a carbon peak due to the carbon in the MWCNT, a copper peak due to the TEM copper grid, and an iron peak due to the filling inside the MWCNTs. The Sm and N peaks are not showing in the EDX spectrum as expected but there is a strong evidence of their presence in Mössbauer spectroscopy.

The $^{57}$Fe Mössbauer spectroscopy measurement was taken in transmission geometry with constant acceleration drive at 20 K and 300 K. Spectrometric data was accumulated in 512 channels until a background of at least 106 counts per channel was reached. The spectrometer was calibrated using room temperature spectrum of α-Fe foil.

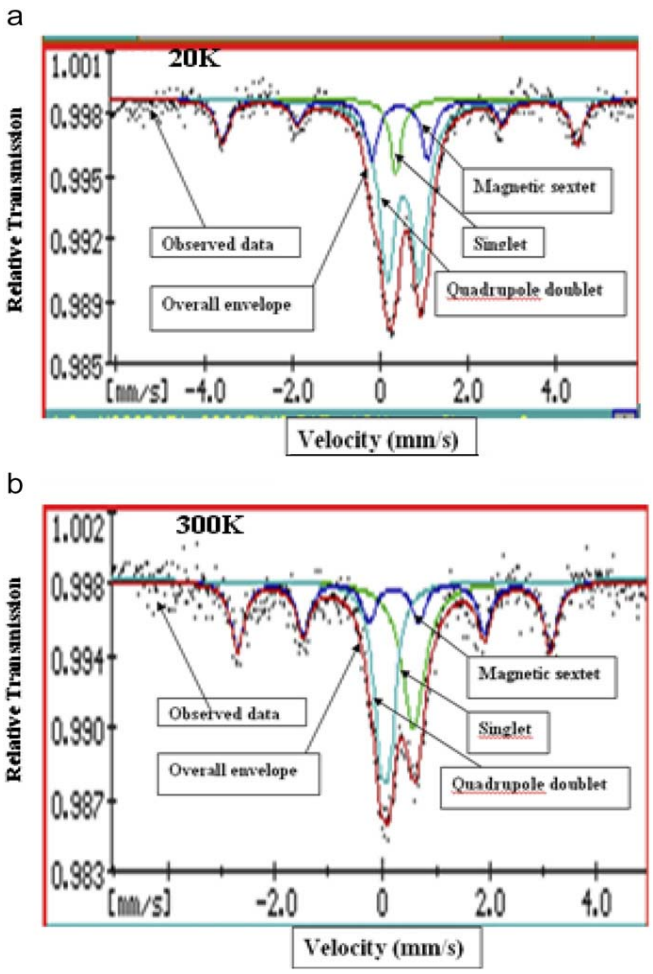



**Fig. 3 Mössbauer spectra of filled MWCNTs. Solid lines are theoretical fit to the observed spectrum in scatter. (a) Mössbauer spectrum at 20K consist of a magnetic sextet of internal hyperfine field 251 kOe and isomer shift 0.43 mm/s, a quadrupole doublet of splitting 0.73 mm/s and isomer shift 0.51 mm/s, and a singlet with isomer shift 0.34 mm/s. (b) Mössbauer spectrum at 300K consist of a magnetic sextet of internal hyperfine field 182 kOe and isomer shift 0.21 mm/s, a quadrupole doublet of splitting 0.18 mm/s and isomer shift 0.04 mm/s, and a singlet with isomer shift 0.58 mm/s.**

All the hyperfine parameters quoted here are with reference to this standard. The spectrum of the sample at 20K (Fig. 3a) is composed of three patterns: a magnetic sextet, a quadrupole doublet, and a singlet. The spectrum of the sample at 300K (Fig. 3b) is also composed of three patterns with different parameter as shown in Table 1.

Table 1 The $^{57}$Fe Mössbauer hyperfine parameters for MWCNTs filled with $Sm_2Fe_{17}N_x$ at temperatures of 20 and 300K

| | 20 K | 300 K |
|---|---|---|
| SEXTET<br>A (%)<br>IS (mm/s)<br>H (KOe) | <br>32<br>0.43<br>251 | <br>38<br>0.21<br>182 |
| QUADRUPOLE<br>A (%)<br>IS (mm/s)<br>QS (mm/s) | <br>59<br>0.51<br>0.73 | <br>32<br>0.04<br>0.18 |
| SINGLET<br>A (%)<br>IS (mm/s) | <br>9<br>0.34 | <br>30<br>0.58 |

Symbols used in this table are: A, percent ratio; IS, isomer shift; QS, quadrupole splitting; and H, hyperfine magnetic field.

The hyperfine field increased at lower temperature by 38% from its room temperature value even though the propensity of the magnetic phase decreased by 16% at low temperature. The presence of the quadrupole in the room temperature (300 K) as well as the 20-K spectra is not due to superparamagnetic state; rather it is due to Fe atoms in a non-magnetic environment with an off cubic symmetry. If it were superparamagnetic state, the doublet would have disappeared at 20 K. It would have transformed into a ferromagnetic state which is characterized by a sextet. For Sm and Fe alloys, the blocking temperature which is the superparamagnetic transition temperature is well above liquid nitrogen temperature 78K [6]. (Seifu et al., 1998). The magnetic hyperfine field at 20K increased to 251 kOe from its room temperature value of 182 kOe; the standard used in this experiment a-Fe has a hyperfine field of 330 kOe. The hyperfine field values as well as the positive values of the isomer shift and quadrupole splitting, Table 1, show close similarity between the measured Mössbauer spectrum in the present study and previous studies [7,8] (Li et al., 1994; Kobayashi et al., 2002) thus strongly suggesting the composition of the filling material to be $Sm_2Fe_{17}N_x$.

A major technical challenge toward that has been the assembly of ordered nanoscale structure and controlled filling. In recent years, there has been success in preparing vertically aligned nanotubes on $SiO_2$ substrate by chemical vapor deposition (CVD)[9]. (Wei et al., 2003). In this paper, we report a single step procedure to fill vertically

aligned multiwalled carbon nanotubes (MWCNTs) with cobalt-ferrite using pulsed laser deposition (PLD).

There has been a previous attempt to fill MWCNTs in aqueous suspension with cobalt ferrite [10] (Keller et al., 2004). Recently, we reported successful chemical filling of MWCNTs with magnetic nanoparticles [11] (Seifu et al., 2008). The present work is the first attempt ever to fill MWCNTs using PLD, a technique which is commonly used to prepare magnetic thin films. The method presented here offers filling technologically useful, aligned MWCNTs, which are suitable for functional devices.

## 2. EXPERIMENT

Vertically aligned MWCNTs were grown by CVD technique on $SiO_2$ substrate following the procedure of Wei et al [9]. This method involves exposing silica structures to a mixture of ferrocene and xylene at 770 $^oC$ for 10 min. The furnace is pumped down to ~200 mtorr in argon bleed and then heated to the temperature of 770 $^oC$. The solution of ferrocene dissolved in xylene (~0.01g/ml) is pre-heated in a bubbler to 175 $^oC$ and then passed through the tube furnace. The furnace is then cooled down to room temperature.
The filling material $CoFe_2O_4$ has a great technological interest because of its large anisotropy and magnetostriction.

The filling was carried out in high vacuum ($2\times10^{-7}$ Torr) where the polycrystalline $CoFe_2O_4$ was ablated with a pulsed excimer laser (KrF) at 1.5 J/cm$^2$ and 3Hz as energy density and repetition rate respectively. During deposition the $SiO_2$ template was heated at 300$^oC$ and the target was rotated in order to ensure its uniform wear. A total of 12,000 shots were fired to fill the nano-tube structure.

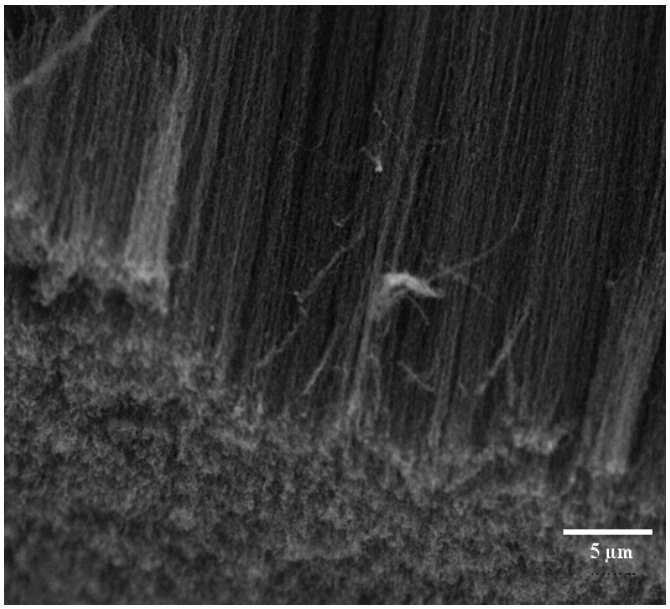
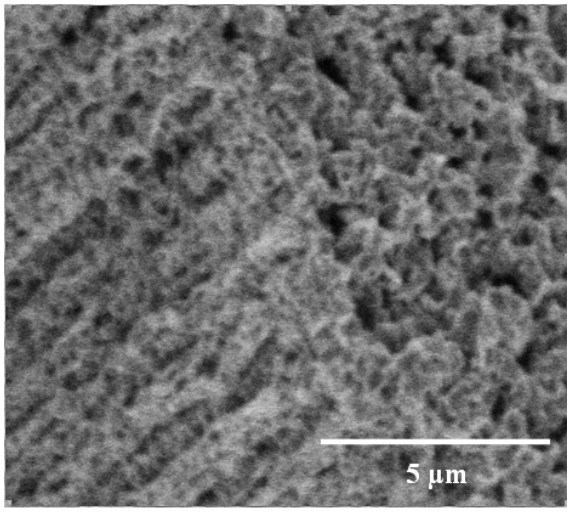



**Fig. 4 SEM micrograph of vertically grown MWNTs on $SiO_2$ before filling.**



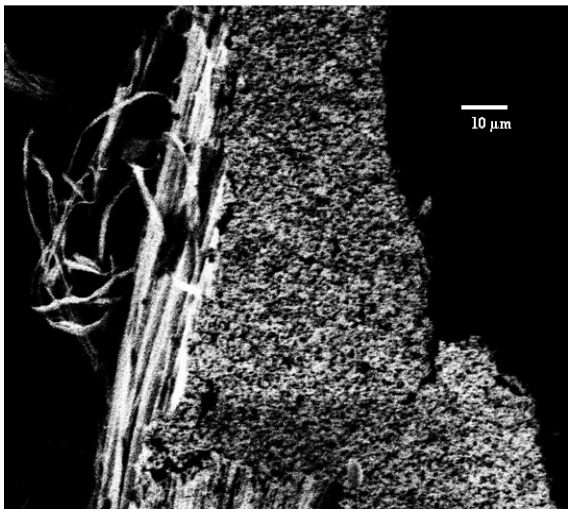




**Fig. 5 Top view SEM image of vertically grown MWNTs on $SiO_2$ filled with $CoFe_2O_4$ by PLD at high resolution in (a) and in lower resolution (b).**

## 3. RESULTS

Scanning electron microscope (SEM) image of the vertically aligned MWCNTs grown on $SiO_2$ substrate before deposition is shown in Fig. 1. As shown in the figure, although the majority of the tubes are aligned vertically, a few are misaligned.

In Fig. 4 SEM of vertical tubes after being filled with cobalt ferrite is shown. The filling depth of the magnetic material in the vertically aligned tubes is not apparent from the SEM image. However, it is possible to obtain this information from the in-plane and out-of-plane magnetization measurements on the sample.

Magnetization measurements were performed with vibrating sample magnetometer, both in-plane and out-of-plane orientation with respect to the sample surface. The result of the magnetization measurements are shown in Fig.

6, depicting the magnetic moment as a function of applied field. The hysteresis loop in solid line corresponds to the in-plane and that with scatter points correspond to the out-of-plane magnetization. As is clear from Fig. 6 both loops indicate reasonable coercivity estimated at 0.4 T. However, the magnetic anisotropy appears to be randomly oriented (polycrystalline) since both loops exhibit the same hysteresis. The unique difference between the in-plane and out-of-plane magnetizations is the sharing produced by the demagnetizing field in the perpendicular direction.

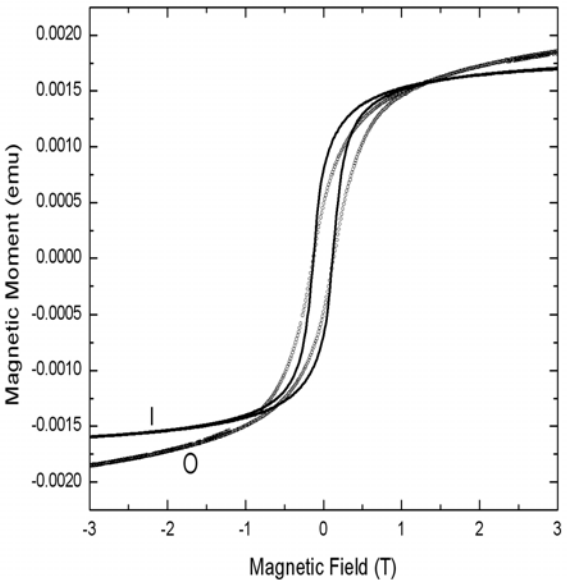



**Fig. 6 Magnetization of the cobalt ferrite nanoparticles filled, vertically aligned MWCNTs. The solid lines represent in-plane and scatter plots represent out-of -plane magnetization.**

## 4. SUMMARY

In summary, we have, for the first time, used pulsed laser deposition technique for high-yield magnetic nanoparticles filling of vertically aligned carbon nanotubes. The magnetization measurements suggest polycrystallinity of the filled magnetic nanoparticles, as evidenced from the randomly oriented magnetic anisotropy. We believe that our present work further extends the applications of CNT-based materials in electronics technologies.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